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Abstract
We have studied thermal expansion of the surface layers of the hexagonally reconstructed Au (001) surface using a classical Molecular Dynamics (MD) simulation technique with an Embedded Atomic Method (EAM) type many-body potential. We find that the top-most hexagonal layer contracts as temperature increases, whereas the second layer expands or contracts depending on the system size. The magnitude of expansion coefficient of the top layer is much larger than that of the other layers. The calculated thermal expansion coefficients of the top-most layer are about -4. 93 ´ 10 -5 Å / K for the (262 ´ 227) Å cluster and -3.05 ´ 10 -5 Å / K for (101 ´ 87) Å cluster. The Fast Fourier Transform (FFT) image of the atomic density shows that there exists a rotated domain of the top-most hexagonal cluster with rotation angle close to 1° at temperature T < 1000K. As the temperature increases this domain undergoes a surface orientational phase transition. These predictions are in good agreement with previous phenomenological theories and experimental studies.

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THERMODYNAMIC BEHAVIOR OF NANO-SIZED GOLD CLUSTERS ON THE (001) SURFACE

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Abstract. We have studied thermal expansion of the surface layers of the hexagonally reconstructed Au (001) surface using a classical Molecular Dynamics (MD) simulation technique with an Embedded Atomic Method (EAM) type many-body potential. We find that the top-most hexagonal layer contracts as temperature increases, whereas the second layer expands or contracts depending on the system size. The magnitude of expansion coefficient of the top layer is much larger than that of the other layers. The calculated thermal expansion coefficients of the top-most layer are about $-4.93 \times 10^{-5} \ Å/K$ for the $(262 \times 227) \ Å$ cluster and $-3.05 \times 10^{-5} \ Å/K$ for $(101 \times 87) \ Å$ cluster. The Fast Fourier Transform (FFT) image of the atomic density shows that there exists a rotated domain of the top-most hexagonal cluster with rotation angle close to 1° at temperature T < 1000K. As the temperature increases this domain undergoes a surface orientational phase transition. These predictions are in good agreement with previous phenomenological theories and experimental studies.

Key words. Molecular Dynamics (MD) simulation, surface reconstruction, surface orientational phase transition, surface thermal expansion

Subject classification. Computational Nano-Materials

1. Introduction. In last few decades there have been extensive studies of surface reconstruction and phase transitions on noble metals and semiconductor surfaces both theoretically [1-3] and experimentally [4-6]. It is now well known that the top-most layer of the Au (001) surface is reconstructed into a hexagonal lattice with (5×*m*) reconstruction patterns where *m* is an integer between 20 and 30. The reconstructed layer is slightly (~3.5%) contracted, distorted and buckled. The rotated domains with rotation angles θ ≈ 1° are found experimentally [7-9]. These rotated domains undergo orientational phase transitions at the temperature around $T \approx 0.75T_m$ where T_m is the bulk melting temperature.

In this paper, we use the MD simulation technique to study the surface properties and calculate the thermal expansion coefficients of the Au (001) surface. We find that the interlayer distance between the top-most hexagonal layer and the second layer, d_1, decreases as the temperature increases, whereas between the second layer and the third layer, d_2, decreases or increases depending on the size of the cluster. The calculated thermal expansion coefficients for the interlayer distance are about $-3.05 \times 10^{-5} \ Å/K$ for $(101 \times 87) \ Å$ cluster and $-4.93 \times 10^{-5} \ Å/K$ for $(262 \times 227) \ Å$ cluster. The Fast Fourier Transform (FFT) image of the atomic density shows that there exists a rotated domain of the top-most layer with rotation angle close to 1° at the temperature T < 1000K. For the

temperature above 1000K the unrotated domain is found to be stable. These findings are in good agreement with previous theoretical studies [10-13] and experimental results [7-9].

2. Method. We use a classical Molecular Dynamics (MD) simulation technique with a modified Verlet algorithm [14] to simulate surface structures and dynamics as a function of temperature. The Embedded Atomic Method (EAM) type many-body potential [15-17],

$$E = \sum_i F[\mathbf{r}_i] + \frac{1}{2}\sum_{i \neq j} V(r_{ij}), \qquad (2.1)$$

is employed for interatomic interactions between Au atoms where the $F[\rho]$ is the embedding function, $V(r_{ij})$ is a two-body interaction potential, and $r_{ij} = |\vec{r}_i - \vec{r}_j|$. The charge density,

$$\mathbf{r}_i = \sum_{j(\neq i)}^{N} \mathbf{r}_a(r_{ij}), \qquad (2.2)$$

is the sum of all atomic charges from neighboring atoms j at the position of ith atom. The spline fitted functions and parameters for Au atoms can be found elsewhere [17].

Our system consists of one fixed (001) layer and two movable (001) layers. On top of these layers, one hexagonal movable layer with 1225 ~ 8281 atoms is placed. We choose the hexagonal top-most layer because our earlier study [10-11] showed that the hexagonal top-most layer is the most stable one in Au (001) surface. The sizes of the second layer and below are much larger than the top-most layer so that the boundary of these layers does not affect the top layer atoms. The usual periodic boundary condition is not applied in this simulation to avoid unwanted boundary effects [10-11].[4]

For a given temperature the lattice constant of the fixed layer is set to the bulk lattice constant at the corresponding temperature, and the movable layers are equilibrated to the required temperature for about 10,000 time steps. After the equilibrium process the thermodynamic quantities are calculated for another 10,000 time steps.

For the sake of convenience we use the MD units in the simulation where ε=3.78eV, σ=2.89Å, and $t_0 = (m\sigma^2/\varepsilon)^{1/2}$ are chosen, respectively, as the units of the energy, length and time. Here m is the mass of a gold atom. The one MD time step is given by $\Delta t = 0.001\, t_0$, where $t_0 = 2.13 \times 10^{-13}$ sec for Au atoms.

3. Results. In Fig. 1 we plot the interlayer distance between the hexagonal layer and second square lattice layer, d_1, as a function of temperature for the cluster size of $(262 \times 227)\, \text{Å}$ (solid circles) and $(101 \times 87)\, \text{Å}$ (open circles). The layer distances for both clusters decrease as the temperature increases. The calculated thermal expansion coefficients in the direction normal to the surface are about $-3.05 \times 10^{-5}\, \text{Å}/K$ for the smaller cluster and $-4.93 \times 10^{-5}\, \text{Å}/K$ for the larger cluster.

Fig. 2 shows the interlayer distance d_2 between the second (square lattice) layer and the third layer as a function of temperature for the cluster size of $(262 \times 227)\, \text{Å}$ (solid circles) and $(101 \times 87)\, \text{Å}$ (open circles). The

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[4] The periodic boundary may not be applicable to this system at all since our system has two different symmetries (hexagonal symmetry on the top layer and square symmetry on the second layer and below).

layer distance d_2 for the smaller cluster (open circles) increases slightly while it decreases for the larger cluster (solid circles) as the temperature increases. However the overall changes are much smaller than that of the d_1. Here we note that, in actual simulation, the second layer (and below) are much larger than the top-most layer cluster to avoid edge effects, but the d_2 is calculated by taking the average of the z distance over the atoms that are beneath the hexagonal layer. The rest of the second layer (i.e., the part in the second layer without the hexagonal layer on top) is contracted more than that for atoms with the hexagonal layer on the top.
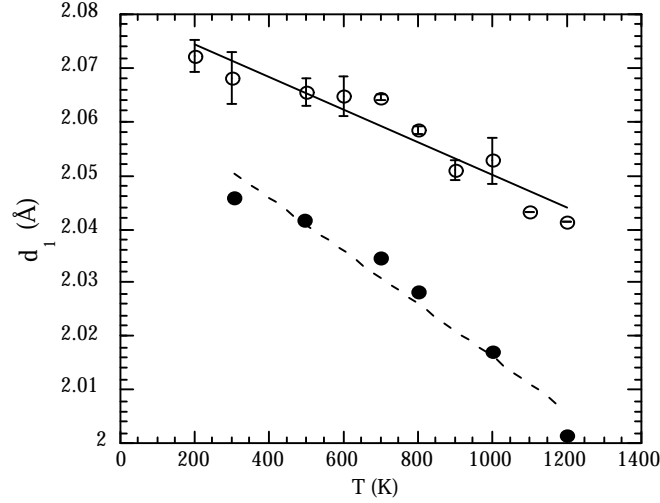

Figure 1: The interlayer distance d_1 as a function of temperature for the cluster size of (262×227) Å (solid circles) and (101×87) Å (open circles). The solid and dashed lines are the linear least square fits.
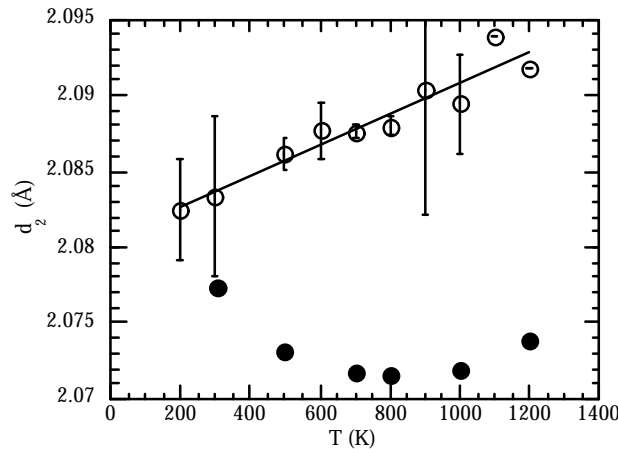

Figure 2: The interlayer distance d_2 as a function of temperature for the cluster size of (262×227) Å (solid circles) and (101×87) Å (open circles).
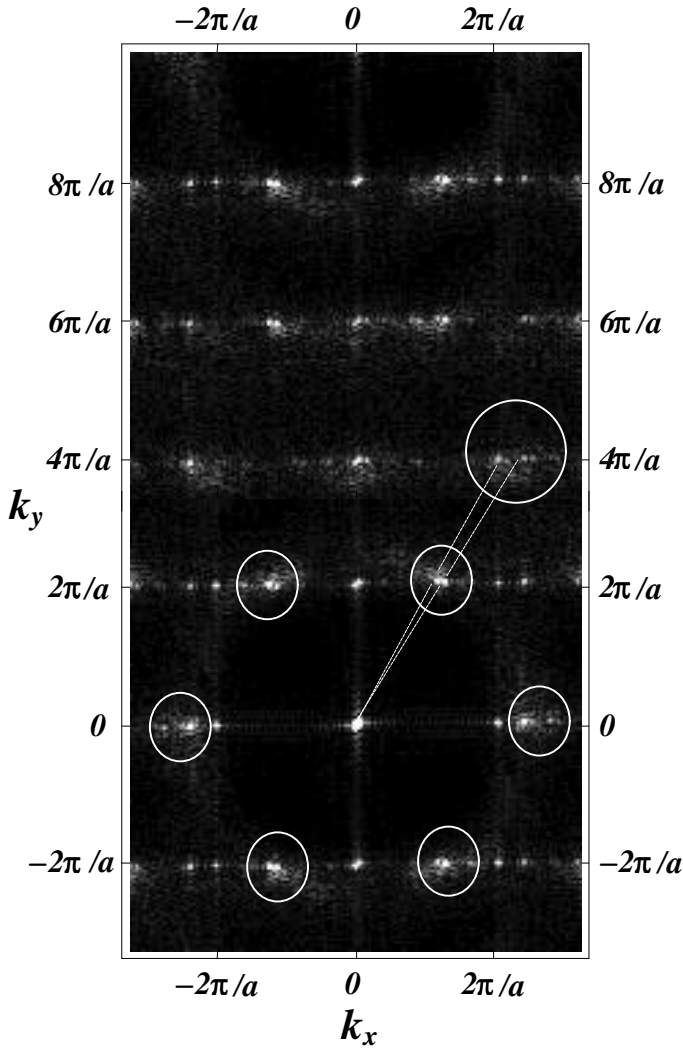
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Figure 3: The FFT image of atomic density for the top-most layer cluster of size (101×87) *Å* at temperature T=300K. The dotted lines are the guides to the eye for rotation angle. The peaks in the white circles represent the hexagonal peaks.

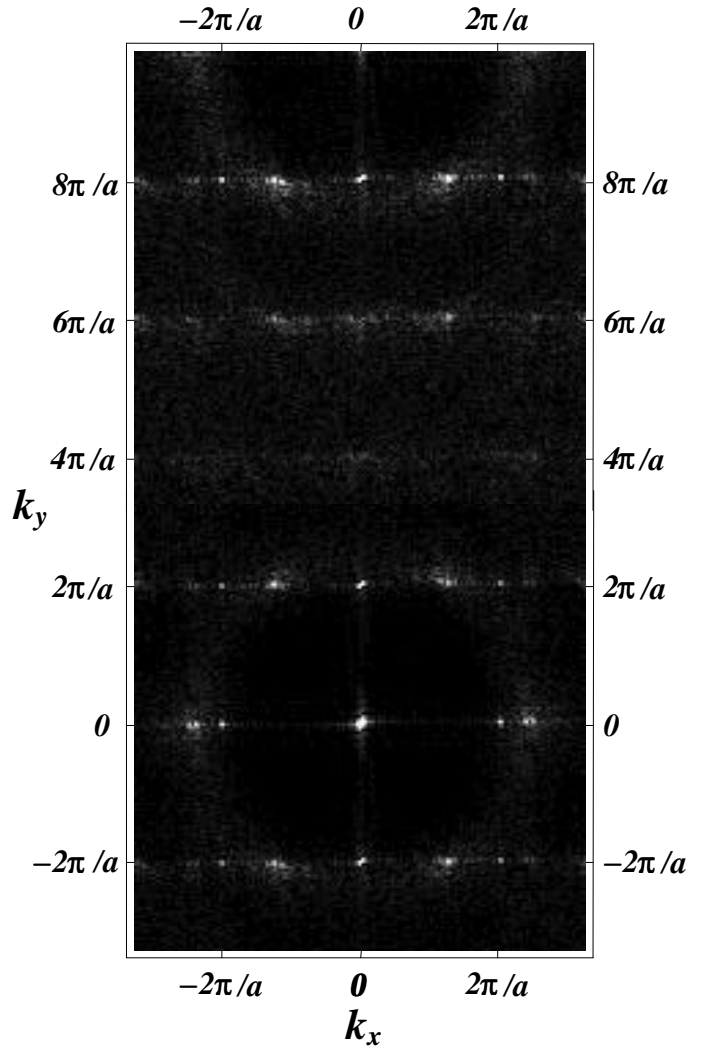*Figure 4:* The density plot of FFT image of atomic density for the cluster size of (101×87) *Å* at temperature T=1200K.

In Fig. 3 we show the density plot of the Fast Fourier Transform (FFT) of the atomic density for the top-most layer cluster of (101×87) *Å* at temperature T=300K. The hexagonal symmetry peaks are clearly shown in the bottom half of the figure. Because of the square lattice underneath the cluster the square symmetry peaks are also visible in the figure. We notice that the hexagonal peaks split in two peaks (see, for example, inside of the white circles in the figure) indicating that the rotated domains coexist with unrotated domains. The separation of the two peaks is very small, i.e., the rotation angle is very small. The rotation angle is about $\theta \approx 1°$. These rotated domains may undergo an orientational phase transition.

In Fig. 4 we plot the same FFT images as in Fig. 3 at the temperature T=1100K. The lattice structure of the top-most layer is still maintained at this temperature, but, with a careful inspection (especially, at second-order peaks in the upper half of the graph), the peaks from the rotated domains are significantly suppressed. The rotated domains

become unstable at high temperature, and an orientational phase transition from the rotated domain to unrotated domain at temperature around T ≈ 1000K is expected.

4. Conclusion. We have studied thermodynamic behavior of the hexagonal top-most layer of Au (001) surface using a MD simulation technique. We calculate the interlayer distances as a function of temperature. We find that the layer distance, d_1, between the top-most layer and second layer is contracted as the temperature increases whereas the second layer distance, d_2, decreases or increases depending on the cluster size. The thermal expansion coefficients are $-3.05 \times 10^{-5} \, Å / K$ for $(101 \times 87) \, Å$ and $-4.93 \times 10^{-5} \, Å / K$ for $(262 \times 227) \, Å$ clusters. The FFT images of the atomic density show that the rotated domains with rotational angles $\theta \approx 1°$ coexist with the unrotated domains in the top layer. As temperature increases these rotated domains undergo a phase transition into unrotated domains. Our findings are in very good agreement with experiments and previous theories.

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